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**High Pressure NMR and Electrical Conductivity Studies Of
Gel Electrolytes Based on Poly(acrylonitrile)**

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HIGH PRESSURE NMR AND ELECTRICAL CONDUCTIVITY STUDIES OF GEL
ELECTROLYTES BASED ON POLY(ACRYLONITRILE)

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The effect of high pressure on electrical conductivity and NMR in gels prepared from lithium or sodium perchlorate, ethylene carbonate, dimethyl carbonate and poly(acrylonitrile) (PAN) has been determined. The corresponding liquids were also studied. Complex impedance studies at frequencies from 10 to 10^8 Hz and NMR measurements of T_1 were carried out as a function of pressure up to 0.25 GPa. Activation volumes for NMR relaxation and ionic conductivity were calculated from the variable pressure data. Both activation volumes were found to be approximately the same in the liquids. For the gels, however, the NMR activation volumes are the same or lower than for the liquid while the electrical conductivity pressure dependences are larger. The implications of these results are discussed in terms of possible effects of the PAN on the ionic solvation shell.

Key words: high pressure, electrical conductivity, nuclear magnetic resonance, gels, complex impedance

INTRODUCTION

Recent advances in lithium battery research have led to the development of gel electrolytes, which consist of a liquid electrolyte immobilized in a polymeric matrix such as poly(acrylonitrile) (PAN) [1,2] or poly(methylmethacrylate) (PMMA) [3]. These gels retain most of the high conductivity characteristic of the liquid phase, but also are mechanically stable enough to form free-standing films. The liquid electrolyte component typically consists of a lithium salt such as LiAsF₆ dissolved in an aprotic solvent such as propylene carbonate (PC) or a mixture of PC and ethylene carbonate (EC). The ion transport mechanism in these composite materials appears to be similar to that of the corresponding liquid electrolyte because the conductivity of the gel is not much lower than that of the liquid. However, the specific nature of the microscopic environment of the Li⁺ ions remains open to question. That is, do they remain completely solvated by EC/PC, with the host polymer providing only a rigid non-interacting matrix, or does the host polymer play an important role in the network structure of the gel and, perhaps, even in the cation transport mechanism? For example, the possibility that the cations could be at least partly solvated by functional groups of the host polymer (e.g. the polar nitrile group in PAN) has been raised by comparing dielectric constants of EC/PC mixture with and without PAN [4].

Previous investigations in our laboratory have addressed this question for PAN- or PMMA-based gel electrolytes by utilizing ⁷Li and ²³Na nuclear magnetic resonance (NMR) techniques [4-6]. Although it was not conclusively demonstrated that the cations interact directly with the host polymer, the presence of microscopic regions of pure liquid electrolytes could be ruled out. The dynamic environment of the cations, probed by temperature-dependent NMR line width and spin-lattice relaxation (T_1) measurements, was found to be

significantly different in the liquid and the gel. Moreover, variations in NMR behavior among different gel samples are strongly correlated with the glass transition temperature (T_g) of the gel, as in the case of polyether-based electrolytes.

In order to obtain additional insight into the possible influence of the host polymer on ion transport, electrical conductivity and cation (^{7}Li and ^{23}Na) NMR measurements as a function of hydrostatic pressure have been undertaken. Employing pressure as the thermodynamic variable has the advantage of yielding activation *volumes*, in much the same way that variable temperature data yield activation energies. The activation volume is a measure of the volume dilatation required for the ions or molecules to move through the material. In this work, we compare conductivity and NMR spin-lattice relaxation data for gel electrolytes with data obtained for the corresponding liquid electrolytes.

From the point of view of long range ionic transport, it is obviously the conductivity results that are most relevant. However, as will be shown, the NMR T_1 data provide information which is essential for understanding both the environs and motion of ions in these materials.

EXPERIMENTAL DETAILS

Gel samples were synthesized from reagent-grade PC (Burdick and Jackson), dimethyl carbonate (DMC, Fluka), PAN (Polysciences, Inc.; 1.5×10^5 g/mole average molecular mass), and different lithium salts, LiClO_4 (Alfa), LiAsF_6 (Lithco), or the sodium salt NaClO_4 (Aldrich). Reference liquid electrolytes were prepared with the following molar ratios of constituents: EC (6), DMC (3), LiClO_4 (1); a second electrolyte prepared with LiAsF_6 ; and a third with NaClO_4 . Three different gels containing LiClO_4 were prepared: sample #1 molar

composition was EC (6), DMC (3), PAN (1) and LiClO₄ (1); the amount of PAN was doubled and tripled for samples #2 and #3, respectively. Two additional gels were prepared with the same molar ratios as sample #3 (i.e. EC (6), DMC (3), PAN (3) and salt (1)), but with LiAsF₆ (sample #4) and NaClO₄ (sample #5). The constituents were further purified and dried, and then combined and cast according to the procedures described in reference 5. For the Li-salt gels, the constituents were mixed together and heated to ~120 to 130°C before complete dissolution of the PAN was achieved, whereas the Na gel required considerably less heating (to about 100°C). The gels containing less PAN (samples #1 and #2) were more homogeneous in appearance than the higher PAN content LiClO₄ sample (#3), but the corresponding NaClO₄ sample (#5) turned out as a clear homogeneous and free-standing, although somewhat sticky, film.

For the NMR measurements, the gels were wrapped in a polyurethane sheath, placed in a radiofrequency (rf) coil and immersed in the pressure transmitting fluid (*Fluorinert FC-77*, 3M Co.) inside a stainless steel pressure vessel. The connection between the rf coil and the tuning capacitors mounted external to the vessel was achieved with a double high pressure feed-through. Liquid samples were enclosed in a two-piece cylindrical teflon cell with pressure transmitted via the piston action of a movable teflon plug. Pressure was generated by a hand-pumped hydraulic system (*Enerpac*) and measured with a 12" *Heise* gauge. The pressure vessel was placed in a 4.7T superconducting magnet and spin-lattice relaxation (T₁) measurements, using both saturation and inversion recovery sequences, were performed at 23°C as a function of applied hydrostatic pressure.

The electrical conductivity of the gels at room temperature in a vacuum was determined using a liquid cell described elsewhere [7]. For the high pressure measurements, the samples were sealed inside latex rubber tubing and

consequently isolated from the pressure fluid (*Spinesstic* 22). Stainless steel electrodes projected through the ends of the rubber tubing into the sample. The electrodes were then clamped onto the closure plug of the high pressure vessel used previously to measure the effect of high pressure on the electrical conductivity of ion conducting polymers [8]. The equivalent parallel capacitance and resistance of the sample were then determined using a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer. All data were then transformed to the complex impedance, $Z^* = Z' - jZ''$.

RESULTS

NMR

Lithium-7 NMR T_1 values for the three LiClO₄-containing gels and the LiClO₄ liquid electrolyte are plotted as a function of pressure in Fig. 1. The data for gel #3 is almost indistinguishable from that corresponding to the liquid. This may at first seem counterintuitive because gel #3 has the highest concentration of PAN, however this sample was also noted to be opaque and inhomogeneous in appearance. Thus it is concluded that sample #3 is phase-separated to a sufficient degree that it yields liquid-like T_1 values. The other gels (#1 and #2) do exhibit distinct T_1 values, in comparison to the liquid.

Previous work on Li-salt containing liquid and gel electrolytes has shown that the T_1 minima of both liquids and gels occur well below room temperature (and the present measurements were taken at room temperature). Thus, decreasing T_1 implies increasing the ionic correlation time. As expected, the application of high pressure further increases the correlation time, resulting in the observed trend of T_1 decreasing with increasing pressure. For the purpose of

relating these results more directly to the transport process, it is useful to define the effective activation volume:

$$\Delta V = -kT \left(\frac{d \ln T_1}{dp} \right) \quad (1)$$

for the case of spin-lattice relaxation mechanisms. The results are summarized in Table I.

It is found that activation volumes calculated from Eq. 1 do not exhibit a large change in going from the liquid to the gel, even for the gels (#1 and #2) that have different T_1 values from the liquid (i.e. the slopes of the T_1 vs. P curves are not much different).

Sodium-23 T_1 vs. pressure values for the NaClO_4 gel (sample #5) and reference liquid electrolytes are plotted in Fig. 2. There is a marked decrease in T_1 going from the liquid to the gel. The relatively larger effect observed in the NaClO_4 system compared with the LiClO_4 system coincides with the observed physical homogeneity of the sodium gel compared to the lithium gel at the highest concentration. However, activation volumes obtained from the slopes of T_1 vs. pressure data are not much different in the gel and the liquid.

Electrical Conductivity

Typical results for the electrical studies of the liquid and gel electrolytes are shown in Fig. 3 in the form of a complex impedance diagram. All data exhibit at least a small portion of a slightly depressed semicircular arc. Slightly depressed semicircular arcs are also observed in "traditional" ion conducting polymers [8]. In addition, electrode and interface effects are observed at the lowest frequencies. The low frequency data, which are dominated by electrode and interface effects, will not be considered further in the present paper.

The bulk resistance, R , was obtained from the intercept of the arc (or position of the minimum value of Z'') with the Z' axis. The conductance, $G=1/R$, was calculated from the intercept. In the case of the atmospheric pressure data, the conductance was transformed to the electrical conductivity, σ , via:

$$\sigma = \ell / GA \quad (2)$$

where A is the area of the sample and ℓ is the length. It was found that the sodium and lithium arsenate gels had conductivities of about 1.8×10^{-3} and 2.1×10^{-3} S/cm, respectively. The conductivity for the liquids...

The results for the variation of the conductance with pressure are shown in Figs. 4-6. The slopes from best-fit straight lines were calculated and are listed in Table I. The pressure variation of the electrical conductivity can be calculated from:

$$\left(\frac{d \ln \sigma}{dp} \right)_T = \left(\frac{d \ln G}{dp} \right)_T + \frac{\chi_T}{3} \quad (3)$$

where χ_T is the isothermal compressibility. The compressibility for either of the materials does not seem to be available. However, the compressibility for most liquids is on the order of $0.8\text{-}1.2 \text{ GPa}^{-1}$ [9]. Consequently, an approximate correction of $\chi_T/3 \approx 0.3 \text{ GPa}^{-1}$ was applied to the data and the results are listed in Table I. Finally, those values were used to calculate an activation volume via:

$$\Delta V = -kT \left(\frac{d \ln \sigma}{dp} \right) \quad (4)$$

and the results are listed in Table I.

In all cases, the conductivity activation volumes for the gel are larger than for the liquid. In the case of the LiClO₄ sample, the values is only slightly larger while the values for the NaClO₄ sample is 60% larger. The results for the LiAsF₆ gel are far more dramatic, exhibiting nearly a three-fold increase over the liquid. Unfortunately, NMR data for this sample are unavailable at the present time.

DISCUSSION

It is interesting that the activation volumes in the liquids obtained from NMR and conductivity measurements are all approximately 11 cm³/mol. This is significant because the two kinds of measurements probe motions on timescales that can differ by many orders of magnitude. Similar agreement has been noted for proton transport in perfluorosulfonic acid membranes containing water [10]. This result implies that the motions being probed by both experiments are the same for the liquids.

For the gels, on the other hand, the activation volumes obtained from the two techniques are significantly different. That is not surprising since it is clear that there is a significant difference between the liquid and the gels. The first evidence for a difference between the liquids and the gels is that, as is apparent from Figs. 1 and 2, T₁ at atmospheric pressure in the non-phase separated gels is shorter than T₁ in the related liquids. This is indicative of restricted local motion in the gels relative to the liquid. Consequently, the difference in *activation volumes* in the gels can be understood because local motions which can contribute to NMR relaxation may not necessarily contribute to long range transport as reflected in ionic conductivity. This implies that there is no *a priori* reason to expect that the activation volumes extracted from T₁ and conductivity measurements will be the same.

In fact, there is no reason to expect that the activation volumes extracted from ^{7}Li NMR to be consistent with those from ^{23}Na NMR. The reason is that spin-lattice relaxation for ^{7}Li is driven primarily by high frequency (i.e. around the NMR Larmor frequency) fluctuations of the $^{7}\text{Li} - ^{1}\text{H}$ magnetic dipole-dipole interaction arising from protons in the solvent molecules and quadrupole relaxation plays a relatively minor role [11]. For ^{23}Na , on the other hand, there is a large quadrupole interaction. Consequently, it is significant that the NMR activation volumes for the LiClO_4 and NaClO_4 gels, and liquids for that matter, are so similar.

Finally, the fact that the conductivity activation volumes *increase*, in going from the liquid to the gel are consistent with the NMR results which show that local mobility is impeded in the gels. The reason, of course, is that an increase in activation volume implies that more volume is required (more dilatation of the material is required) for ion motion and this is most simply interpreted as increased impedance to ion motion.

In prior work [4] it was suggested that PAN could possibly compete with EC (or DMC) for ion solvation, but that the most likely interaction would still be with the solvent molecules because of their higher concentration. In the present materials, even the highest concentration PAN gels have a mole factor of three more EC/DMC than PAN. The NMR activation volume results suggest that the ions are primarily solvated by the EC/DMC and that rearrangement or motion of the solvation shell, which is necessary for ionic transport, involves a similar change in volume in both the liquid and the gel. The fact that the T_1 's and conductivity values decrease in going from the liquid to the gel, however, show that the microscopic viscosities differ in the two media even though the solvation shells are similar. Thus the PAN, whose purpose is to provide *macroscopic* dimensional stability, influences short-range ionic dynamics (i.e. at time scales

on the order of the Larmor frequency), although apparently not by direct bonding interactions with the cation. A similar conclusion has been drawn from recent ^{19}F NMR pulsed field gradient diffusion measurements in liquid and "gelled" polyethers, which show that anion diffusion coefficients are smaller in the gels, but that the activation *energies* are similar in the two media [12].

The LiAsF₆ results are intriguing and clearly warrant further study, in particular NMR studies. Also, a more systematic investigation, involving other gels optimized for homogeneity is warranted. These studies are in progress.

CONCLUSIONS

The effect of high pressure on the electrical conductivity and NMR in gels prepared from lithium or sodium perchlorate, ethylene carbonate and dimethyl carbonate and poly(acrylonitrile) (PAN) has been determined. The corresponding liquids were also studied. NMR measurements of T_1 and complex impedance studies at frequencies from 10 to 10^8 Hz were carried out as a function of pressure up to 0.25 GPa on the same materials. Activation volumes for NMR relaxation and ionic conductivity were calculated from the variable pressure data. Both activation volumes were found to be approximately the same in the liquids. For the gels, however, the NMR activation volumes are the same or lower than for the liquid while the electrical conductivity pressure dependences are larger. Finally, atmospheric pressure T_1 values are found to be much lower in the gel than in the liquid. All results are consistent with a model where ion motion is more impeded in the gel than in the liquid.

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Table I. Summary of the pressure dependence of ion motion of various electrolytes.

	$\left(\frac{d\ln G}{dp}\right)_T$ (GPa) ⁻¹	$\left(\frac{d\ln \sigma}{dp}\right)_T$ (GPa) ⁻¹	$\left(\frac{d\ln T_1}{dp}\right)_T$ (GPa) ⁻¹	ΔV cm ^{3/mol}	ΔV cm ^{3/mol}
Sodium Liquid	-4.8	-4.5	-4.9	11.2	12.2
Sodium Gel	-7.3	-7.0	-3.6	17.4	9.0
LiClO ₄ Liquid	-4.9	-4.6	-4.1	11.4	10.2
LiClO ₄ Gel (2)	-5.8	-5.5	-2.1	13.7	5.2
LiClO ₄ Gel (1)			-4.1		10.2
LiClO ₄ Gel (3)			-3.7		9.2
LiAs Liquid	-5.4	-5.1		12.7	
LiAs Gel	-12.2	-11.9		29.6	
				Cond.	NMR

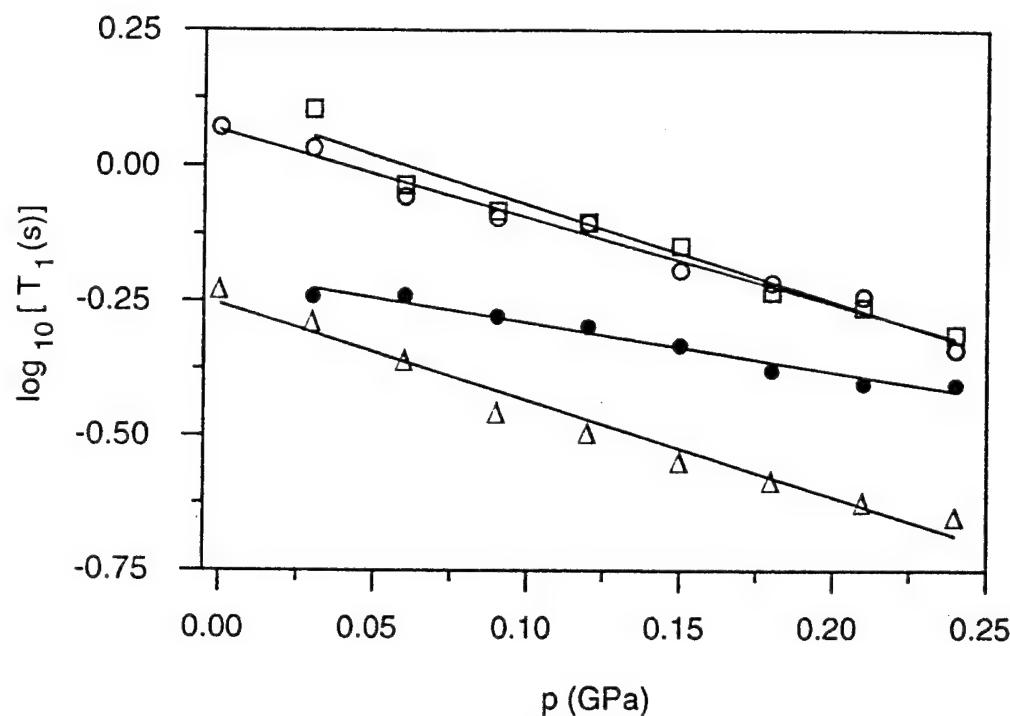


Figure 1. Pressure dependence of ^7Li T_1 for the PAN based gel (gel #2: solid circles; gel #1: triangles; gel #3: open circles) and associated liquid (squares) containing LiClO_4 . Also shown are the best-fit straight lines.

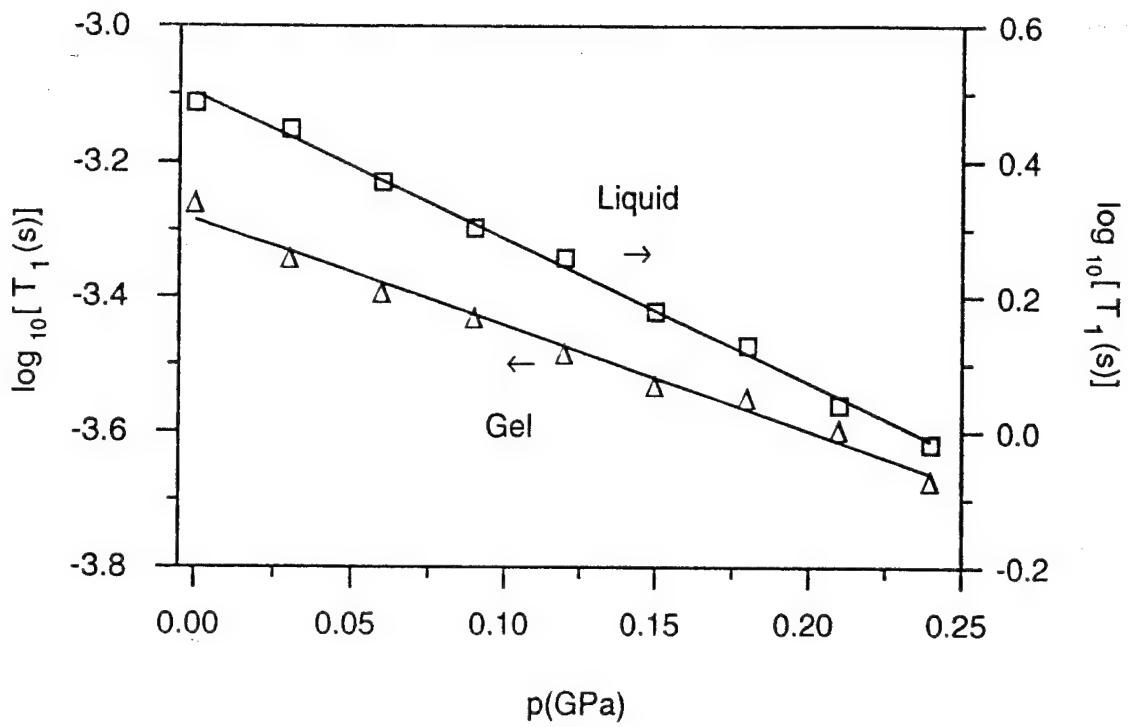


Figure 2. Pressure dependence of ^{23}Na T₁ for the PAN based gel (triangles) and associated liquid (squares) containing NaClO₄. Also shown are the best-fit straight lines.

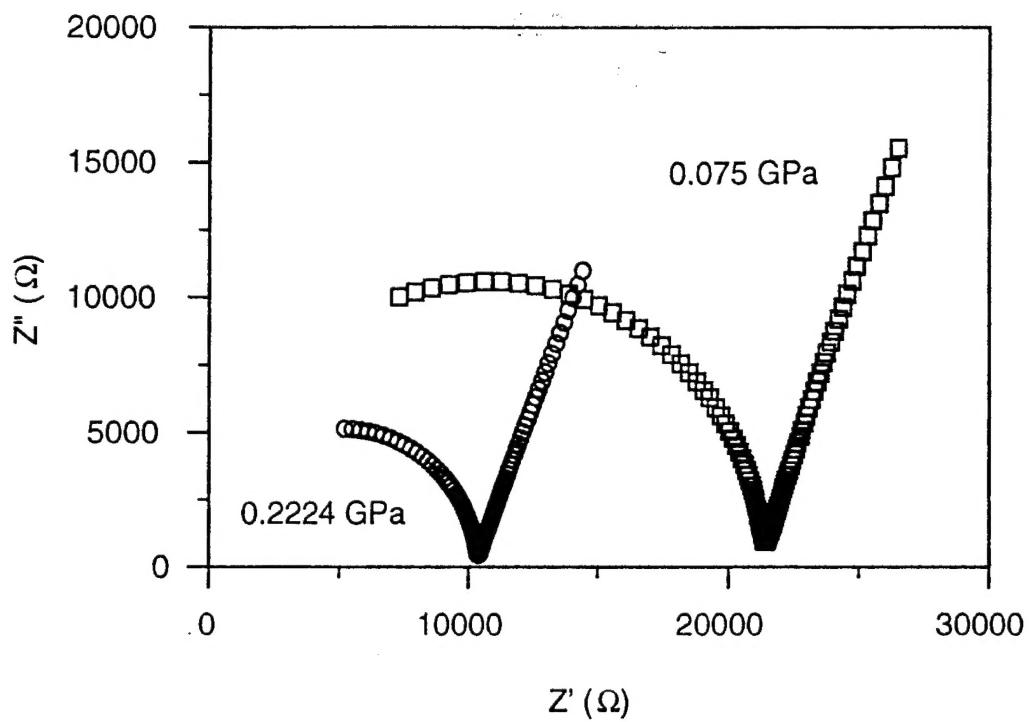


Figure 3. Complex impedance diagrams at two pressures for NaClO₄ liquid. The squares (smaller arc) are the data at 0.2224 GPa and the circles are the data at 0.075 GPa. The frequencies are 10^4 Hz to 10^8 Hz from right to left.

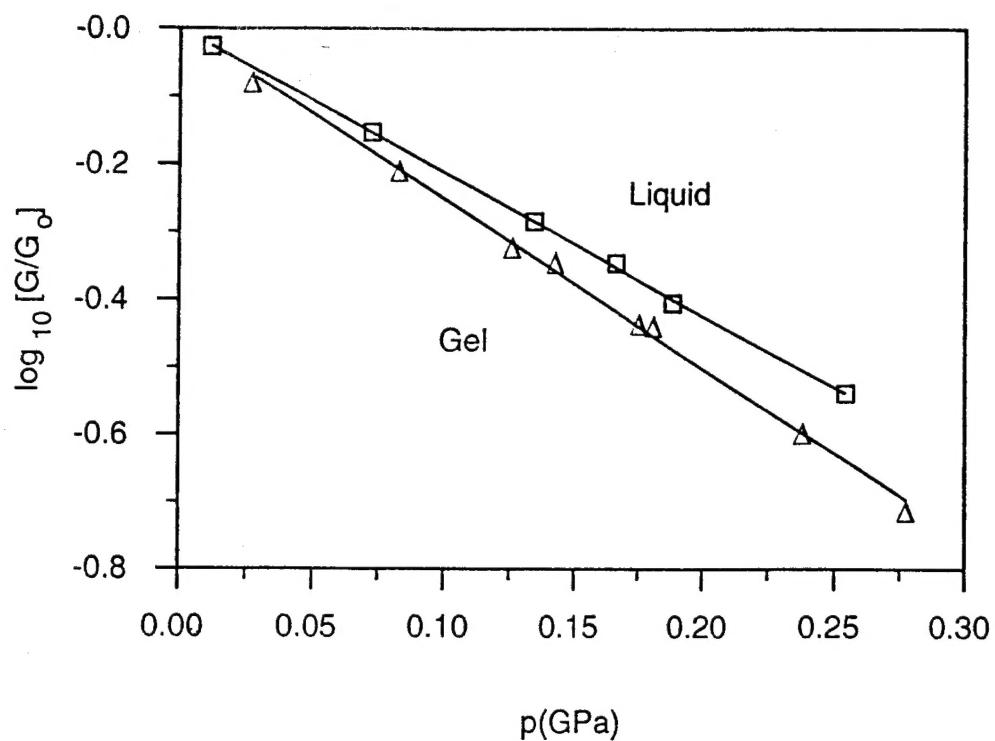


Figure 4. Electrical conductivity vs. pressure at room temperature (about 298 K) and various pressures for the PAN based gel (triangles) and associated liquid (squares) containing LiClO_4 . Also shown are the best-fit straight lines.

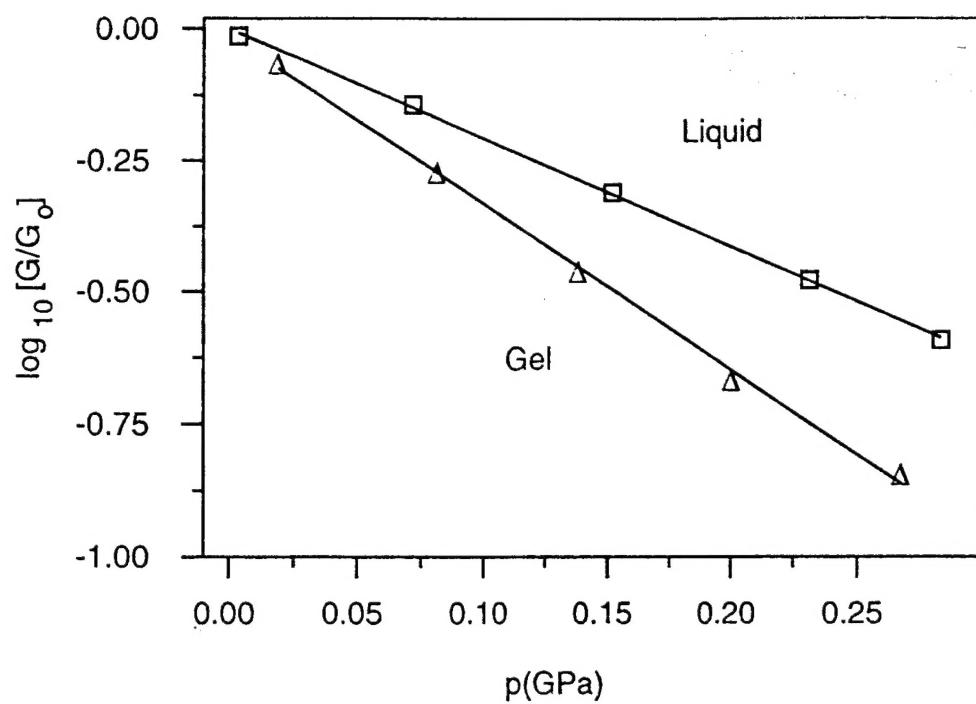


Figure 5. Electrical conductivity vs. pressure at room temperature (about 298 K) and various pressures for the PAN based gel (triangles) and associated liquid (squares) containing NaClO_4 . Also shown are the best-fit straight lines.

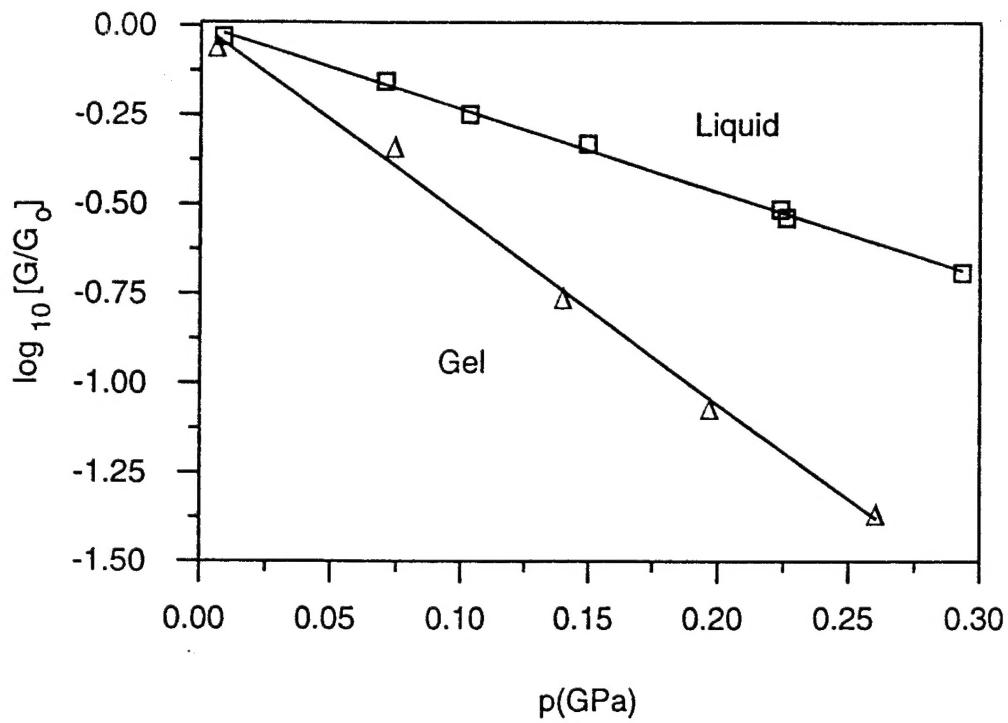


Figure 6. Electrical conductivity vs. pressure at room temperature (about 298 K) and various pressures for the PAN based gel (triangles) and associated liquid (squares) containing LiAsF₆. Also shown are the best-fit straight lines.